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PROCESS FOR PRODUCING ORGANICALLY MODIFIED AEROGEL

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## PROCESS FOR PRODUCING ORGANICALLY MODIFIED AEROGEL

The invention concerns a method for producing organically modified aerogels.

Aerogels, especially ones with porosities over 60% and densities under  $0.6 \text{ g/cm}^3$ , have extremely low thermal conductivity and for this reason are used as heat insulation materials, as described in EP-A-0 171 722, for example.

Aerogels in the broader sense, i.e., in the sense of "gel with air as dispersion agents," are produced by drying a suitable gel. The term "aerogel" in this sense includes aerogels in the narrower sense, xerogels and cryogels. In this case a dried gel is meant as aerogel in the narrower sense when the liquid of the gel is largely removed at temperatures above the critical temperature and starting with pressures above the critical pressure. If, in contrast, the liquid of the gel is removed under subcritical conditions, for example while forming a liquid-vapor interface, the resulting gel is in many cases also called a xerogel.

When the term aerogel is used in this application, it means aerogels in the broader sense, i.e., in the sense of a "gel with air as dispersion agent."

In addition, aerogels can basically be divided into inorganic and organic aerogels.

Inorganic aerogels have been known since 1931 (S. S. Kistler, Nature 1931, 127, 741). Since that time aerogels have been made from many different starting materials. For example,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SnO}_2$ ,  $\text{Li}_2\text{O}$ ,  $\text{CeO}_2$  and  $\text{V}_2\text{O}_5$  aerogels as well as mixtures of these have been produced (H. D. Gesser, P. C. Goswami, Chem. Rev. 1989, 89, 765 ff).

Also, organic aerogels of many different starting materials, such as melamine formaldehyde, have been known for a number of years (R. W. Pekala, J. Mater. Sci. 1989, 24, 3221).

Inorganic aerogels can be made in different ways.

For one,  $\text{SiO}_2$  aerogels can be made, for example, by acid hydrolysis and condensation of tetraethyl orthosilicate in ethanol. This results in a gel that can be dried by supercritical drying while maintaining its structure. Production methods based on this drying technique, are known, for example, from EP-A-0 396 076, WO 92/03378 and WO 95/06617.

A basic alternative to this method, which involves very high costs and high processing risks, is offered by a method for subcritical drying of  $\text{SiO}_2$  gels. The  $\text{SiO}_2$  in this case is produced by acid hydrolysis of tetraalkoxysilanes in a suitable organic solvent by means of water. After exchange of the solvent for a suitable organic solvent, the resulting gel is converted with a silylation agent in an additional step. The resulting  $\text{SiO}_2$  gel can then be dried in air from an organic solvent. In this way aerogels with densities under  $0.4 \text{ g/cm}^3$  and porosities over 60% can

be produced. A production method based on this drying technique is described in detail in WO 94/25149.

Moreover, the above described gels can be mixed with tetraalkoxysilane in an alcohol-water solution before drying and aged in order to increase the gel network strength, as disclosed in WO 92/20623.

However, the tetraalkoxysilanes that are used in the above described methods as starting material are an extraordinarily high cost factor. A considerable reduction of costs can be achieved by using water glass as starting material for the production of the  $\text{SiO}_2$  gels. For this silicic acid can be made, for example, from an aqueous water glass solution with the aid of an ion exchange resin and then polycondensed to an  $\text{SiO}_2$  gel through the addition of a base. After exchange of the aqueous medium for a suitable organic solvent the resulting gel is then reacted with a chlorine-containing silylation agent in an additional step. The resulting  $\text{SiO}_2$  gel, which has been modified on the surface with, for example, methylsilyl groups, can then be dried in air, likewise from an organic solvent. The preparation method based on this technique is disclosed in DE-A-43 42 548.

Moreover, the use of chlorine-free silylation agents in the production of subcritically dried aerogels is described in DE-C-19502453.

In addition, an organofunctionalization by means of appropriate silylation agents in the production of subcritically dried aerogels is described in DE-A-19534198.

Moreover, DE-A-19541279 describes the preparation of hydrophobic subcritically dried aerogels. In this case the costly silylation agents, which confer permanent hydrophobicity on the future aerogel, are intentionally omitted in the production process and instead an aerogel with oxygen-bound hydrophobic surface groups is prepared using less expensive alcohols. However, the described aerogel is only hydrophobic for a brief time because of this.

DE-A-19541715 and DE-A-19541992 describe an improved method in which a silica sol with a pH value  $\leq 4.0$  is prepared from an aqueous water glass solution with the aid of an acid and then, in a second step, polycondensed to an  $\text{SiO}_2$  gel through the addition of a base. The acid that is used forms a sparingly soluble salt with the cations of the water glass, which is separated in an additional process step. The aerogel is obtained by a subsequent surface modification and subcritical drying.

With all of the methods for subcritical drying of  $\text{SiO}_2$  gels based on water glass that are known from the prior art, the required  $\text{SiO}_2$  gel is prepared in two steps. In a first step an acid silica sol is prepared from water glass either with the aid of an acid ion exchange resin or an acid. In this case a pH  $\leq 4.0$  is established to ensure that the silica sol is stable for a short time. In a second step the silica sol is then mixed with a base for formation of an  $\text{SiO}_2$  gel.

These two step methods have the disadvantage that they are cost intensive on the one hand and are difficult to control on the other. The difficulty of control derives, among other things, from the fact that the initially formed silica sol is only stable for a short time and the sol structure is continuously changing.

For this reason the task of this invention was to make available a method with which organic modified aerogels can be produced in a simple way.

This task is solved by a method for producing organically modified aerogels in which

a) an  $\text{SiO}_2$  gel is obtained from an aqueous water glass solution with the aid of at least one organic acid, an inorganic acid and/or a hydrochloric acid solution via the intermediate step of a silica sol,

b) the gel obtained in step (a) is washed with an organic solvent until the water content of the gel is  $\leq 5$  wt%,

c) the gel obtained in step (b) is surface-silylated, and

d) the surface-silylated gel obtained in step (c) is dried under subcritical conditions, which is characterized by the fact that the silica sol is prepared by adding the aqueous solution to the acid with rapid mixing of the two solutions, and the silica sol formed as the intermediate stage has a pH in the range of 4 to 8, where the  $\text{SiO}_2$  gel is formed through the formation of a silica sol with simultaneous polycondensation.

Preferably the pH is  $\geq 4$  and  $\leq 6$ . The advantage of the method in accordance with the invention lies in the fact that the  $\text{SiO}_2$  gel forms in a matter of seconds in one step through the formation of a silica sol with simultaneous polycondensation. Moreover, the aerogels produced in accordance with the invention are chiefly permanently hydrophobic.

Generally a 6 to 25 wt% (with respect to the  $\text{SiO}_2$  content) sodium and/or potassium water glass solution is used as the water glass solution in step (a). A 10 to 25 wt% water glass solution is preferred and a 10 to 18 wt% water glass solution is especially preferred. In addition, the water glass solution can contain up to 90 wt%, with respect to  $\text{SiO}_2$ , compounds of zirconium, aluminum, tin, gallium, indium and/or titanium that are capable of condensation, preferably zirconium, aluminum and/or titanium compounds.

Generally 1 to 15 wt% acids, preferably 1 to 10 wt% acids, are used as the acids. Preferred acids are sulfuric, phosphoric, hydrofluoric, oxalic and hydrochloric acids. Hydrochloric acids, especially 3 to 7 wt% hydrochloric acid is especially preferred. Mixtures of said acids can also be used.

If hydrochloric acid solutions are used, aluminum salts above all are suitable, in particular aluminum sulfate and/or chloride.

Besides the actual mixing of the water glass solution and the acid it is, moreover, also possible initially to add a part of the acid to the water glass solution, until a pH of  $\geq 8$  is obtained, and in an additional step to established the above pH value of the sol and/or initially to add a part of the water glass solution to the acid until the pH is  $\leq 4$  and in an additional step to establish the final pH value. In this way it is possible to vary the ratio of the flows of water glass solution/acid over a very broad range.

After mixing the two solutions preferably a 5 to 12 wt%  $\text{SiO}_2$  gel should be obtained. A 6 to 9 wt%  $\text{SiO}_2$  gel is particularly preferred.

In order to ensure mixing of the water glass solution and salt that is as thorough as possible before the  $\text{SiO}_2$  gel is formed, the two solutions should have a temperature between 0 and  $30^\circ\text{C}$ , especially preferably between 5 and  $25^\circ\text{C}$  and in particular between 10 and  $20^\circ\text{C}$ , preferably separately from each other. If an acid that forms sparingly soluble salts with the sodium and/or potassium ions of the water glass is used, the temperature should not be reduced so strongly that these salts of precipitate in crystalline form. This could result in defects occurring in the  $\text{SiO}_2$  structure that forms.

The rapid mixing of the two solutions takes place in devices known to the specialist, such as stirred vessels, mixing nozzles and static mixers. Semicontinuous or continuous methods, for example mixing nozzles, are preferred.

Optionally a shaping step, for example by spray forming, extrusion or droplet formation, can take place simultaneously in step (a).

Before step (b) the gel can preferably be aged, namely in general at 20 to  $100^\circ\text{C}$ , preferably at 40 to  $100^\circ\text{C}$ , in particular at 80 to  $100^\circ\text{C}$ , and at a pH of 2.5 to 11, preferably 4 to 8. The time needed for this is in general 1 sec to 12 h, preferably 1 sec to 5 h, and especially preferably 1 sec to 2 h.

Before step (b) the gel is preferably washed with water, especially preferably until the wash water that is used is free of electrolytes. If aging of the gel is carried out, the washing can in this case be conducted before and/or after the aging, where the gel in this case is preferably washed after the aging.

Mixtures of water and a solvent from step (b) can also be used for washing. The water content should, however, preferably be high enough that the salts do not crystallize out in the pores of hydrogel.

In order to remove the sodium and/or potassium ions as much as possible, the hydrogel can also be washed with a mineral acid before, during and/or after the washing with water. Preferred mineral acids in this case are the mineral acids indicated in step (a) as preferred.

In step (b) the gel obtained from step (a) is washed with an organic solvent until the water content of the gel is  $\leq 5$  wt%, preferably  $\leq 3$  wt%, and especially preferably  $\leq 1$  wt%. In general, aliphatic alcohols, ethers, ester or ketones as well as aliphatic or aromatic hydrocarbons are used as solvents. Mixtures of said solvents can also be used. Preferred solvents are methanol, ethanol, acetone, tetrahydrofuran, ethyl acetate, dioxane, pentane, n-hexane, n-heptane and toluene. Acetone is especially preferred as solvent. Mixtures of said solvents can also be used. In addition, the water can first be washed out with a water-miscible solvent, for example an alcohol, acetone or THF, and then this solvent can be washed out with a hydrocarbon. Pentane or n-heptane are preferably used as hydrocarbons.

In step (c) the solvent-containing gel is reacted with a silylation agent. Preferably silanes of the formula  $R^1_{4-n}SiCl_n$  or  $R^1_{4-n}Si(OR^2)_n$  with  $n = 1-3$ , where  $R^1$  and  $R^2$ , independent of one another, are the same or different and are  $C_1$ - $C_6$  alkyl, cyclohexyl or phenyl, are preferably used as silylation agents. Isopropenoxysilanes and silazanes are also suitable. Trimethylchlorosilane is especially preferably used. Moreover, all of the silylation agents known to the specialist can be used. The reaction is carried out in general at 20 to 100°C, preferably 20 to 70°C, preferably in a solvent. Optionally, the silylation can be accelerated by a catalyst, for example an acid or base.

Before step (d) the silylated gel is preferably washed with a protic or aprotic solvent until the unreacted silylation agent is largely removed (residual content  $\leq 1$  wt%). Suitable solvents are those mentioned in step (b). Similarly, the solvent, indicated there as preferred are also preferred here.

In step (d), the silylated and preferably washed gel is dried under subcritical conditions, preferably at temperatures of  $-30$  to  $200^\circ\text{C}$ , especially preferably  $0$  to  $100^\circ\text{C}$ , and at pressure preferably from  $0.001$  to  $20$  bar, especially preferably  $0.01$  to  $5$  bar, in particular  $0.1$  to  $2$  bar, for example by radiation, convection and/or contact drying. The drying is in general carried out until the gel has a residual solvent content of less than  $0.1$  wt%. The aerogels obtained after drying are permanently hydrophobic.

In another embodiment the gel can, in each case according to use, be subjected to an additional strengthening of its network before the silylation in step (c). This is done by reacting the resulting gel with a solution of an orthosilicate of the formula  $R^1_{4-n}Si(OR^2)_n$  that is capable of condensation, preferably an alkyl and/or aryl orthosilicate, where  $n = 2$  to  $4$  and where  $R^1$  and  $R^2$ , independent of one another are hydrogen atoms, linear or branched  $C_1$ - $C_6$  alkyl, cyclohexyl or phenyl residues, or with an aqueous silicic acid solution.

In another embodiment the gel can, after the shaping polycondensation in step (a) and/or any subsequent process step, be size-reduced by techniques known to the specialist, such as grinding.

In addition, the opacifiers can be added as additives to the water glass, the acid and/or the sol before preparation of the gel, in particular IR opacifiers to reduce the contribution of radiation to thermal conductivity, for example carbon black, titanium oxide, iron oxides and/or zirconium oxide.

In another embodiment fibers can be added to the water glass, the acid and/or the sol to increase the mechanical stability. Inorganic fibers, for example glass fibers or mineral fibers, organic fibers such as polyester fibers, aramid fibers, nylon fibers or fibers of vegetable origin, as well as mixtures of these can be used as the fiber materials. The fibers can also be coated, for example, polyester fibers that are metalized with a metal such as, for example, aluminum.

The aerogels produced in accordance with the invention find use in particular as heat insulation materials.

The method in accordance with the invention is illustrated below in more detail by means of embodiment examples without being limited by them.

#### Example 1

2043 g of a 5.46 wt% HCl solution cooled to 10°C is mixed by drops with 2043 g of a 16 wt% sodium water glass solution (containing 13 wt% SiO<sub>2</sub> and with an Na<sub>2</sub>O:SiO<sub>2</sub> ratio of 1:3.3) cooled to 10°C. In doing so a pH of 4.7 is established. The hydrogel that forms after a few seconds is aged for 1 h at 85°C. Then it is washed with 3 l warm water and the water is exchanged for acetone with 3 l acetone. Then the acetone-containing gel is silylated with trimethylchlorosilane (10 wt% trimethylchlorosilane per gram of wet gel). The drying of the gel takes place in air (3 h at 40°C, then 2 h at 50°C and 12 h at 150°C).

The resulting gel has a density of 0.12 g/cm<sup>3</sup>, a thermal conductivity of 17 mW/mK, a specific BET surface of 771 m<sup>2</sup>/g and is permanently hydrophobic. C/H/N analysis gives 10.7 wt% C and 3.1 wt% H.

#### Example 2

2500 g of 80% sulfuric acid cooled to 10°C is mixed by drops with 2500 g of a 25.5 wt% sodium water glass solution (containing 13 wt% SiO<sub>2</sub> with an Na<sub>2</sub>O:SiO<sub>2</sub> ratio of 1:3.3) cooled to 10°C. In doing so a pH of 6.3 is established. The hydrogel that forms after a few seconds is aged for 1 h at 85°C. Then it is washed with 3 l warm water and the water is exchanged for acetone with 3 l acetone. Then the acetone-containing solution is silylated with trimethylchlorosilane (5 wt% trimethylchlorosilane per gram of wet gel). The drying of the gel takes place in air (3 h at 40°C, then 2 h at 50°C and 12 h at 150°C).



The resulting gel has a density of  $0.154 \text{ g/cm}^3$ , a thermal conductivity of  $21 \text{ mW/mK}$ , a specific BET surface of  $630 \text{ m}^2/\text{g}$  and is permanently hydrophobic. C/H/N analysis gives 7.7 wt% C and 1.9 wt% H.

The thermal conductivity was measured by the hot wire method (see, for example, O. Nielsson, G. Ruschenpohler, J. Gross, J. Fricke, High Temperatures – High Pressures, Vol. 21, 267-274 (1989)).

### Claims

1. A method for producing organically modified aerogels, in which
  - a) an  $\text{SiO}_2$  gel is obtained from an aqueous water glass solution with the aid of at least one organic acid, an inorganic acid and/or a hydrochloric acid solution via the intermediate step of a silica sol,
  - b) the gel obtained in step (a) is washed with an organic solvent until the water content of the gel is  $\leq 5 \text{ wt}\%$ ,
  - c) the gel obtained in step (b) is surface-silylated, and
  - d) the surface-silylated gel obtained in step (c) is dried under subcritical conditions,
 which is characterized by the fact that the silica sol is prepared by adding the aqueous solution to the acid with rapid mixing of the two solutions, and the silica sol formed as the intermediate stage has a pH in the range of 4 to 8, where the  $\text{SiO}_2$  gel is formed through the formation of a silica sol with simultaneous polycondensation.
2. A method as in Claim 1, which is characterized by the fact that a 6 to 25 wt% sodium and/or potassium water glass solution is used as water glass solution.
3. A method as in Claim 1 or 2, which is characterized by the fact that sulfuric, phosphoric, hydrofluoric, oxalic and/or hydrochloric acid is used as acid.
4. A method as in at least one of the preceding claims, which is characterized by the fact that the temperatures of the water glass solution and acid that are used, independent of one another, lie in the range of 0 to  $30^\circ\text{C}$ .
5. A method as in at least one of the preceding claims, which is characterized by the fact that the gel obtained in step (a) is allowed to age at 20 to  $100^\circ\text{C}$  at a pH of 2.5 to 11 for a period of 1 sec to 12 h before step (b).
6. A method as in at least one of the preceding claims, which is characterized by the fact that the gel obtained in step (a) is washed with water before step (b).
7. A method as in at least one of the preceding claims, which is characterized by the fact that aliphatic alcohols, ethers, esters, ketones, aliphatic and/or aromatic hydrocarbons are used as organic solvents in step (b).

8. A method as in at least one of the preceding claims, which is characterized by the fact that at least one silane of the formula  $R^1_{4-n}SiCl_n$  or  $R^1_{4-n}Si(OR^2)_n$  with  $n = 1$  to  $3$ , where  $R^1$  and  $R^2$ , independent of one another, are the same way or different and are  $C_1$ - $C_6$  alkyl, cyclohexyl or phenyl, is used as silylation agent in step (c).
9. A method as in at least one of the preceding claims, which is characterized by the fact that the surface-silylated gel is washed with a protic or aprotic solvent before step (b).
10. A method as in at least one of the preceding claims, which is characterized by the fact that the silylated step is dried at temperature of  $-30$  to  $200^\circ C$  and pressures of  $0.001$  to  $20$  bar in step (d).
11. A method as in at least one of the preceding claims, which is characterized by the fact that the gel obtained in step (a) is reacted before the surface modification with a solution of an orthosilicate of the formula  $R^1_{4-n}Si(OR^2)_n$  that is capable of condensation, where  $n = 2$  to  $4$  and  $R^1$  and  $R^2$ , independent of one another, are hydrogen atoms, linear or branched  $C_1$ - $C_6$  alkyl, cyclohexyl or phenyl residues, or with an aqueous silicic acid solution.
12. A method as in at least one of the preceding claims, which is characterized by the fact that fibers are added to the water glass solution, the acid and/or the sol.
13. A method as in at least one of the preceding claims, which is characterized by the fact that opacifiers, in particular IR opacifiers, are added to the water glass, the acid and/or the sol.
14. A method as in at least one of the preceding claims, which is characterized by the fact that the resulting gel is size reduced after step (a) and/or any subsequent process step.